AD-A242 314

Technical Report 1441
August 1991

A Review of High-Temperature Superconductivity and the Effect of Chemical Modifications on $Bi_2Sr_2CaCu_2O_8$ and $Bi_2Sr_2Ca_2Cu_3O_{10}$

T. E. Jones
W. C. McGinnis
R. D. Boss
Naval Ocean Systems Center

P. M. Thibado
University of Pennsylvania

91-14137

91 10 2 020

NAVAL OCEAN SYSTEMS CENTER
San Diego, California 92152-5000

J. D. FONTANA, CAPT, USN
Commander

R. T. SHEARER, Acting
Technical Director

ADMINISTRATIVE INFORMATION

Released by
J. C. Hicks, Head
Research Branch

Under authority of
R. H. Moore, Head
ASW Technology
Division

OBJECTIVE

Perform chemical modifications to existing materials that may enhance their superconducting properties and provide insight into the mechanisms responsible for high-temperature superconductivity.

RESULTS

1. Presented a review of high-temperature superconductivity. An overview of superconductivity from its original discovery to the present is also given.

2. Synthesized two sets of samples. One set was based on the structure $Bi_2Sr_2CaCu_2O_8$ and the other on $Bi_2Sr_2Ca_2Cu_3O_{10}$. In both cases, the copper was partially replaced with elements from the first transition row of elements. The replacement was at the level of 5 mol.-% of the transition element for copper. The transition elements used were vanadium (V), manganese (Mn), titanium (Ti), nickel (Ni), zinc (Zn), cobalt (Co), and iron (Fe).

3. Determined the effect of the substitutions on the crystal structure. The change in the lattice spacing for each substituent was determined using x-ray diffraction. The observed changes in lattice parameter scaled well with the atomic radii of the substituents for reasonable substituent valences. This is consistent with the substituent actually replacing copper in the two crystal structures.

4. Measured the superconducting transitions, both resistively and inductively, and determined the suppression of T_c for the transition elements when replacing copper in these two phases. All these substituents reduced the T_c relative to the pure unsubstituted material.

5. Determined that for both phases, vanadium suppressed T_c the least. For $Bi_2Sr_2CaCu_2O_8$, cobalt and iron suppressed T_c the most. For $Bi_2Sr_2Ca_2Cu_3O_{10}$, nickel suppressed T_c the most (cobalt and iron did not go into this phase for copper).

CONCLUSION

1. The suppression of T_c does not correlate with the substituent's position in the periodic table, its ionic radius, its observed magnetic moment, or with its ionization potential.

2. There is a strong correlation between T_c and the occupancy of the $d_{x^2-y^2}$ orbital. The five 'd' orbitals of copper are split in energy in these materials due to the particular crystal symmetry of the copper site. The $d_{x^2-y^2}$ orbital is the highest energy 'd' orbital of copper in this structure. This indicates that the suppression of Tc is

electronic in nature. That is, it is the $d_{x^2-y^2}$ orbitals which contain the electrons responsible for superconductivity in these materials. Altering the occupancy of these levels is important in affecting the superconducting properties of these materials.

Accession For		
NTIS GRA&I	☑	
DTIC TAB	☐	
Unannounced	☐	
Justification		
By		
Distribution/		
Availability Codes		
Dist	Avail and/or Special	
A-1		

DTIC
COPY
INED

ii

CONTENTS

FIGURES

TABLES

CONTENTS (continued)

INTRODUCTION

The discovery of high-temperature superconductivity in 1987 opened the door to new families of materials that previously could not be imagined. These materials, which exhibit superconductivity at temperatures above the standard boiling point of liquid nitrogen (> 77 K), are very different from formerly known superconductors. A distinguishing common feature of all these new materials is that they are all forms of copper oxide. One goal of this project was to investigate the role and the importance of copper in these systems. To accomplish this, up to 5 mole-% of elements from the first transition row of the periodic table (V, Mn, Ti, Ni, Zn, Co, and Fe) were substituted for copper in both of the superconducting phases, $Bi_2Sr_2CaCu_2O_8$ and $Bi_2Sr_2Ca_2Cu_3O_{10}$. The effect of these substitutions on the crystal lattice is documented. Also, evidence is presented that correlates the transition temperature with the electronic structure of the substituent.

BACKGROUND

Judging by the number of articles appearing in the popular press over the past few years, one might guess that superconductivity was a recent discovery. The truth is that superconductivity was discovered in 1911 (Onnes, 1911). This field has had considerable development since 1911 (Gorter, 1964) and, in fact, has been associated with four Nobel Prizes awarded in physics. What is a superconductor? There are many unique properties of superconductors. However, for simplicity and brevity, the following three features of superconductors should be noted (Kittel, 1971):

First, when cooled below its "critical temperature," T_c, a superconductor loses all resistance to the flow of DC electric current. There are no ohmic losses; it is a "perfect conductor" in that sense.

Second, when cooled below its T_c in a modest magnetic field, a superconductor expels essentially all of the magnetic flux inside the material. That is, a superconductor becomes a perfect diamagnet. This is called the Meissner effect. This property of a superconductor does not follow simply from Maxwell's equations of electromagnetism applied to a material with zero resistance. That is, a superconductor is more than just a "perfect conductor." The superconducting state has been shown to be a state where the electrons are paired. The superconducting material undergoes an electronic phase transition at T_c. Because of this, T_c is often referred to as the transition temperature.

Third, the superconducting state has been shown to be a macroscopic quantum state of the electron gas in the material. There are several important consequences of the macroscopic quantum nature of the superconducting state, such as superconducting tunneling (DC and AC Josephson effects) and the quantization of magnetic flux inside a superconducting ring. Also, because of the macroscopic quantum nature of the

1

superconducting state, different regions in a material, or different superconducting regions in a circuit, can exhibit macroscopic quantum interference. The reason this is referred to as macroscopic interference is because these interference phenomena can be observed with standard laboratory instruments, such as by measuring ordinary voltages and currents. Devices using macroscopic quantum interference are called Superconducting Quantum Interference Devices (SQUIDs).

Small-scale applications, using lossless conduction and quantum interference effects, include interconnects in microelectronics for low dispersion, integrated transformers on a chip, infrared detectors, magnetometers and gradiometers, low-power and high-speed logic and memory circuits, analog-to-digital converters, and monolithic millimeter-wave electronic components such as resonators, filters, and delay lines intended for operation in the GHz range of frequencies.

Large-scale applications include magnets and energy-storage systems. The very large current densities attainable in advanced superconductors produce magnetic fields many times larger than those achievable with iron electromagnets. These very small lightweight magnets allow powerful motors and generators to be constructed (in much smaller and lighter packages than by using conventional technology) for applications such as shipboard-propulsion and power-generation systems.

WHAT ARE THE HIGH-TEMPERATURE SUPERCONDUCTORS?

In the context of high-temperature superconductivity, high temperature refers to materials that superconduct above the temperature at which liquid nitrogen boils (77 K). The dramatic breakthrough, started by Bednorz and Müller (1986) with the discovery of $La_{2-x}Sr_xCuO_4$ (T_c = 35 K), is illustrated in figure 1. Within a few months, $YBa_2Cu_3O_7$ had been discovered with a T_c greater than 90 K (Wu et al., 1987). The following year, new materials had been discovered with transition temperatures up to 125 K. One of these two new families of materials is based on the element bismuth, another, with a similar structure, is based on the element thallium (Chu et al., 1988; Sheng et al., 1988). All of these new superconductors are ceramic oxides.

The history line in figure 1 starts in 1911 with the discovery of the first superconducting material, elemental mercury (Hg), with a T_c near 4.2 K. After 60 years of intense research in this field, the highest T_c found prior to the new ceramics was in Nb_3Ge in the 1970s with a T_c of 23 K. The title "BCS" in the figure refers to the microscopic theory of superconductivity published by Bardeen, Cooper, and Schrieffer (1957). The horizontal line in figure 1, indicating the boiling point of liquid nitrogen, marks at least a psychological barrier separating temperature regimes where extreme cryogenics are required (liquid helium), and only moderate cryogenics are required (liquid nitrogen). Liquid nitrogen is readily available, inexpensive, and easy to use, compared with liquid helium.
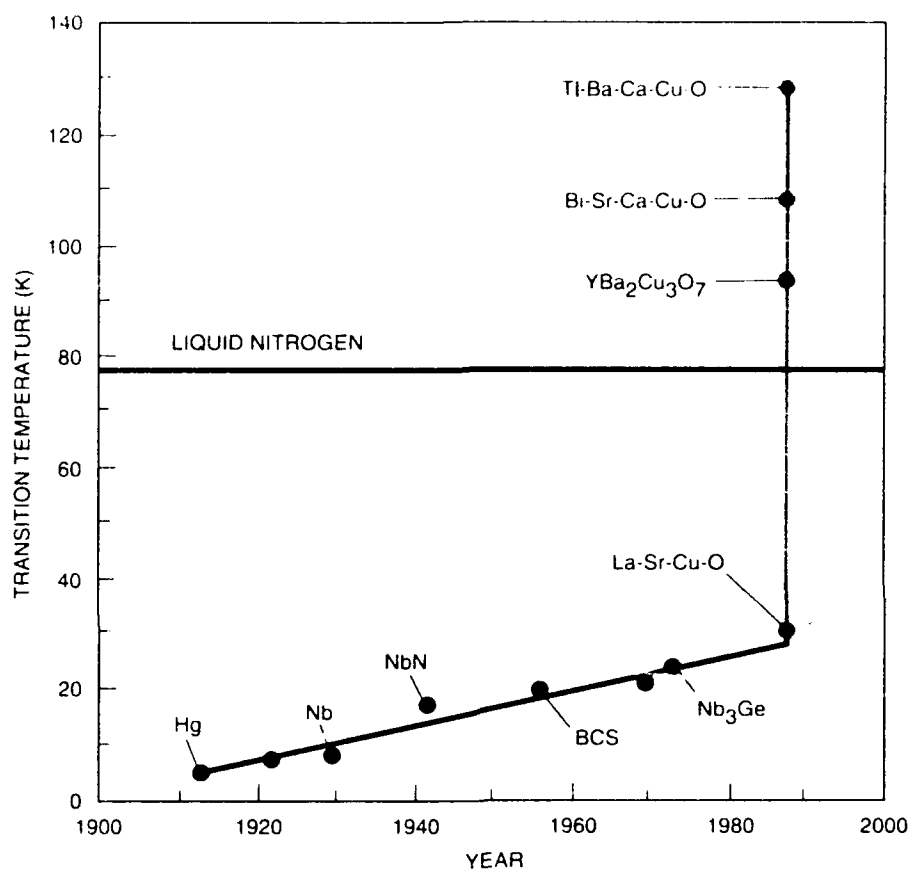
2

Figure 1. A history of superconductivity. The
red symbols highlight the recent developments.

Table 1 gives some perspective on the three most common temperature scales. The table should make it clear why the absolute temperature scale (Kelvin) is used in most cryogenic applications. The references in the table to liquid helium, nitrogen, argon, and oxygen, indicate the temperature where these cryogenic liquids boil at atmospheric pressure.

Table 1. Temperature scales.

	T(K)	T(°C)	T(°F)
Absolute zero	0	−273	−459
Liquid helium	4	−269	−452
Liquid hydrogen	20	−253	−423
T_c of Nb_3Ge	23	−250	−418
Liquid nitrogen	77	−196	−321
Liquid argon	87	−186	−303
Liquid oxygen	90	−183	−297
High T_c ceramics	100	−173	−279
Water freezes	273	0	32
Room temp.	293	20	68
Water boils	373	100	212

So what is different about the new ceramics? To appreciate the difference, a few observations should be made about the previously known superconductors. First, superconductivity is not a rare phenomenon in nature. At least 28 of the metallic elements in the periodic table are superconductors at low enough temperatures. The element with the highest T_c is niobium (T_c = 9.2 K). Second, if one includes simple alloys and intermetallic compounds, the number of known superconductors is in the thousands (virtually all with T_c < 20 K). Third, superconductivity is also known to occur in at least one inorganic polymer (T_c = 0.3 K) (Green, Street, and Suter, 1975), and in several organic crystals (T_c > 10 K) (Ribault et al., 1987).

The principal difference between all these older materials and the new ceramics, aside from the much higher transition temperatures, is that the new materials (with T_c > 77 K) are all copper oxides. The material discussed in some detail below is based on the elements Bi-Sr-Ca-Cu-O. These materials form many phases. However, the two of primary interest in superconductivity are illustrated in figure 2. These materials all possess Cu–O substructures with either square planar or square pyramidal symmetry. The distinguishing feature between the various high T_c phases in this bismuth-based material is the number of Cu-O planes. The general formula for this structure is $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, where 'n' represents the number of adjacent Cu-O planes. The commonly studied phases in this system are $Bi_2Sr_2CuO_6$ (n = 1 and T_c = 20 K), $Bi_2Sr_2CaCu_2O_8$ (n = 2 and T_c = 80 K), and $Bi_2Sr_2Ca_2Cu_3O_{10}$ (n = 3 and T_c = 110 K).

The above example clearly shows that the new ceramic superconductors are very complicated. They all contain at least four elements that must be in the proper stoichiometry and crystal phase. In bulk form, these oxides are all ceramics with all of the mechanical deficiencies associated with other ceramic materials, such as brittleness, lack of ductility, and a low strain-to-failure value. In quality thin-film form, however, the ceramic nature of these materials is not much of a factor in terms of electronic applications.

PARTIAL SUBSTITUTIONS FOR COPPER

Understanding the reasons why these new materials superconduct at such high temperatures has been one of the most active areas of research in solid-state physics. The microscopic quantum mechanical theory of superconductivity, as it applies to all previously known superconductors, is well developed and was the subject of the 1972 Nobel Prize in physics. The extent to which this theory applies to the new materials, if at all, is the subject of current research among the best theoretical physicists around the world. There is currently no consensus one way or the other. Thus, from both an experimental and theoretical point of view, understanding the origins of high-temperature superconductivity is of fundamental and practical importance.

These arguments provided the motivation for the work described below. That is, one of the major experimental objectives is to understand *the role of copper in these materials*. One way to do that is to replace the copper with another element. The difficulty with attempting the total replacement of the copper is that the desired new material generally cannot be made. This leaves the partial replacement of copper as a productive way of ascertaining the most important properties of the copper. To carry out this investigation, candidate replacement elements chemically similar to copper, which will hopefully go into the structure for the copper, must be found. In addition, evidence must be provided that the replacement element does actually go into the crystal structure in place of the copper. Then, the structural and electronic properties of the modified materials must be determined. The elements in the periodic table that seem most likely to substitute for copper are those elements in the first transition row of elements. The elements used were titanium, vanadium, manganese, iron, cobalt, nickel, and zinc. All of these elements, including copper, have a partially filled '3d' shell. They have unique magnetic moments, size, and ionization potentials.
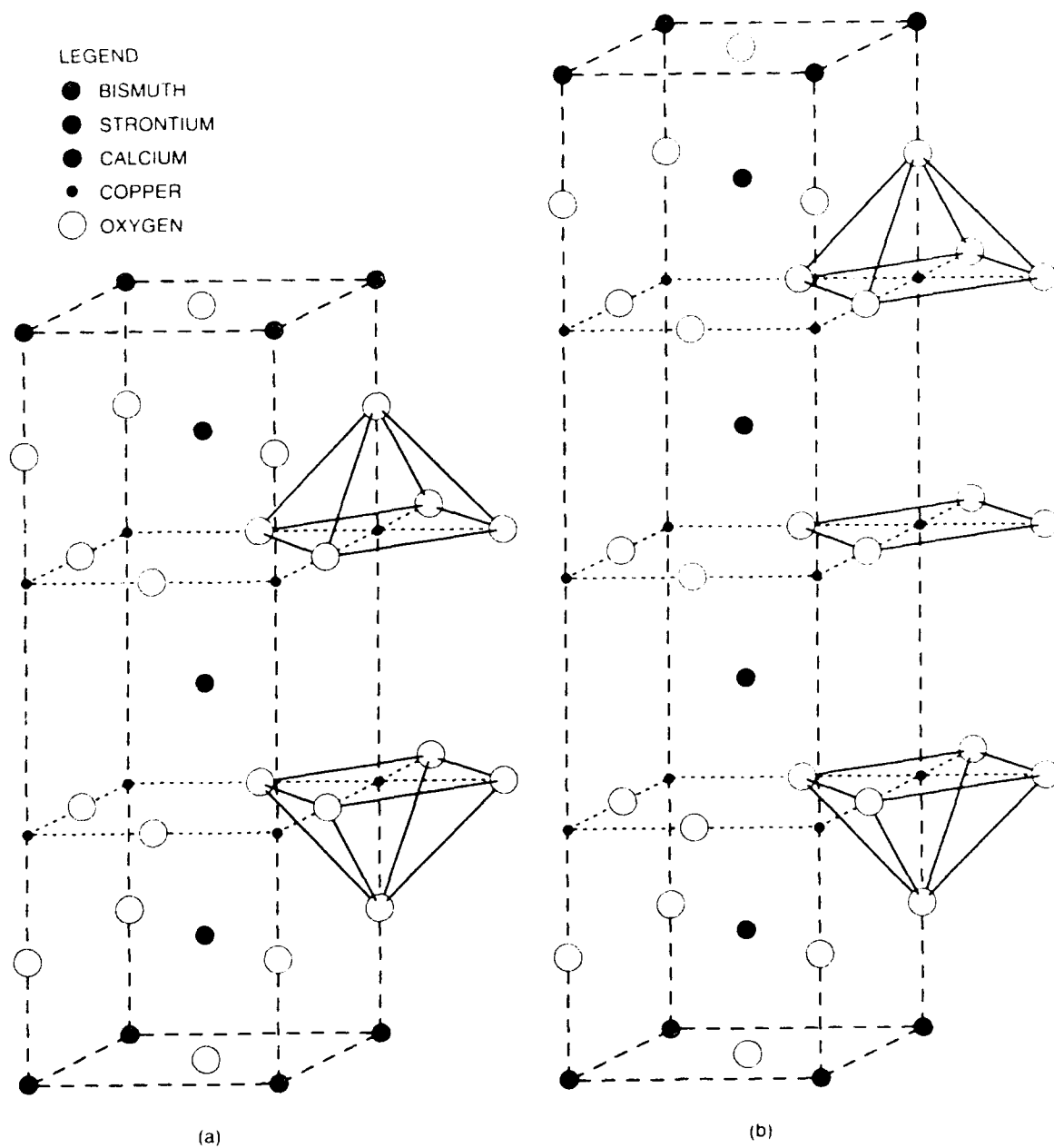
Figure 2. The crystal structures for (a) $Bi_2Sr_2CaCu_2O_8$ and (b) $Bi_2Sr_2Ca_2Cu_3O_{10}$.

LEGEND
- BISMUTH
- STRONTIUM
- CALCIUM
- COPPER
- OXYGEN

(a)

(b)

Details of the sample preparation have been presented elsewhere (Jones et al., 1989; Thibado et al., 1990; Jones et al., 1990). For the sake of brevity, only an outline of the preparation conditions and the results of physical characterization measurements will be given in this article. However, a few observations should be noted Chemical modifications such as those performed in this investigation have to be done very carefully. One complication is that the synthesis conditions necessary to form the desired phase will generally change with the chemistry. These materials are synthesized by sintering for long times (20 to 200 hours) at temperatures close to their melting temperatures (850 to 900 °C). The type of chemical modifications described here can easily change the melting temperature of the material 5 to 20°C. Thus, each composition had to be specially processed. The crystallographic purity of the samples was determined by x-ray diffraction. The goal was to achieve essentially single-phase material, at least with respect to the various superconducting phases described above. The superconducting transitions were also measured both resistively and inductively. Another test of the quality of the final product is the measurement of single, narrow transitions with no evidence of multiple phases.

The final compositions sought for this investigation can be described by the formulae $Bi_2Sr_2Ca(Cu_{0.95}M_{0.05})_2O_8$ and $Bi_2Sr_2Ca_2(Cu_{0.95}M_{0.05})_3O_{10}$, for the 80 K and 110 K phases respectively, where M represents one of the first transition row elements: Ti, V, Mn, Fe, Co, Ni, Cu, or Zn. That is, the goal was to make a 5.0 mole-% partial replacement of the copper. This amount was chosen because it involved a chemical change that was not too severe and perhaps, therefore, achievable. Also, the effects of 5.0 mole-% should be measurable in the crystal structure and in the electronic properties. It has been found that the addition of lead facilitates the growth of the 110 K phase. For this investigation, 20 mole-% lead has been substituted for the bismuth for the 110 K phase only. Some of the lead probably replaces bismuth and perhaps strontium in the structure. The role of the lead replacement is not completely known. For simplicity, the presence of lead is not explicitly shown in the formula $Bi_2Sr_2Ca_2Cu_3O_{10}$.

A major task in this type of investigation is to determine the crystallographic effect of the chemical substitution. That is, one must first show that the substitution has taken place by demonstrating a change in the lattice parameters and, second, determine where in the structure the impurity ion is going based on such considerations as chemical properties and ionic radius.

An additional complication is that these materials contain from four to six different elements and the actual replacement site in the lattice will not always agree with the planned replacement site. In addition to using the x-ray diffraction pattern to characterize the phase composition of these materials, the lattice parameters can also be refined from the observed spectra if one has indexed reflections. For these materials, the largest effect is anticipated in the c-axis direction, that is, the large vertical unit cell distance as

displayed in figure 2. The results of this analysis, for the final materials used in this investigation, are plotted in figure 3(a) for $Bi_2Sr_2Ca(Cu_{0.95}M_{0.05})_2O_8$, and in figure 3(b) for $Bi_2Sr_2Ca_2(Cu_{0.95}M_{0.05})_3O_{10}$. In the figure, the left vertical axis represents the refined c-axis lattice parameter. The right vertical axis represents the change in c-axis spacing with respect to the all-copper control sample. In the figure, the circles with error bars represent the x-ray determined lattice parameter; the other symbols represent the expected lattice parameter based on the substituent's ionic radius, assuming a valence of either 2+ (squares – □) or 3+ (triangles – Δ).

The following observations can be made from figure 3. From figure 3(a), for the $Bi_2Sr_2CaCu_2O_8$ phase, one concludes that all these transition elements enter the crystal structure at the 5 mole-% for copper replacement level. Further, the c-axis lattice parameter scales with the substituent's ionic radius assuming a valence of 2+ for V, Mn, Fe, Co, Ni, and Zn, and a valence of 3+ for Ti. From figure 3(b), for the $Bi_2Sr_2Ca_2Cu_3O_{10}$ phase, only the Ti, V, Zn, and Mn go into the structure in phase-pure form. Also, the c–axis lattice parameter agrees with the substituent's ionic radius assuming a valence of 2+ for Zn, and a valence of 3+ for Ti, V, and Mn. Note also that in figure 3(b) there are fewer data points. The reason is that not all of the substituted materials could be made in this phase in phase-pure form. In particular, the Fe and Co would not go into the $Bi_2Sr_2Ca_2Cu_3O_{10}$ structure at 5 mole-% for Cu, and the Ni would only go in as a mixed phase sample, 90% $Bi_2Sr_2Ca_2Cu_3O_{10}$ and 10% $Bi_2Sr_2CaCu_2O_8$.
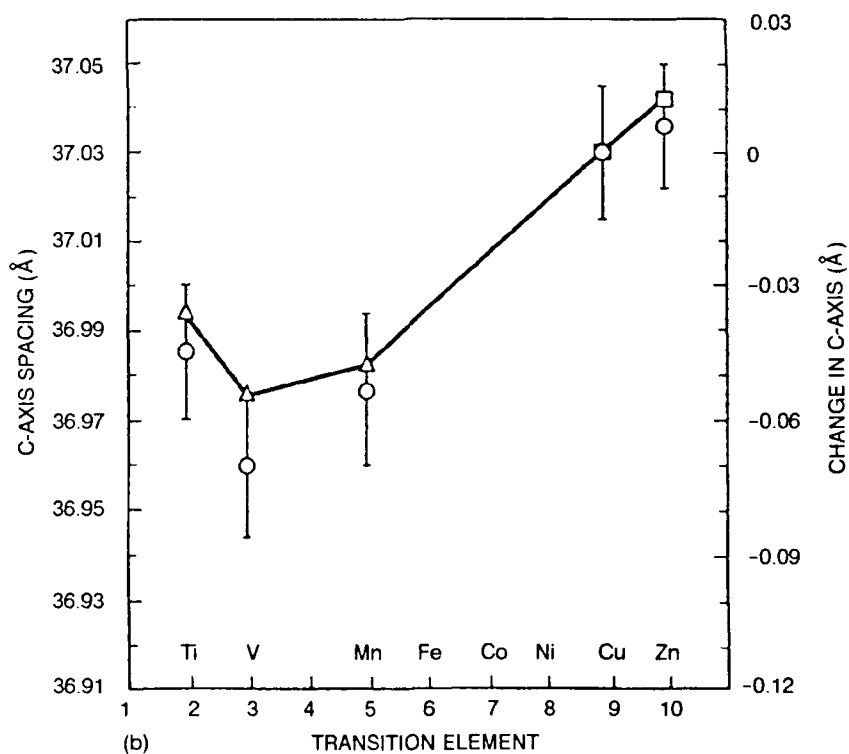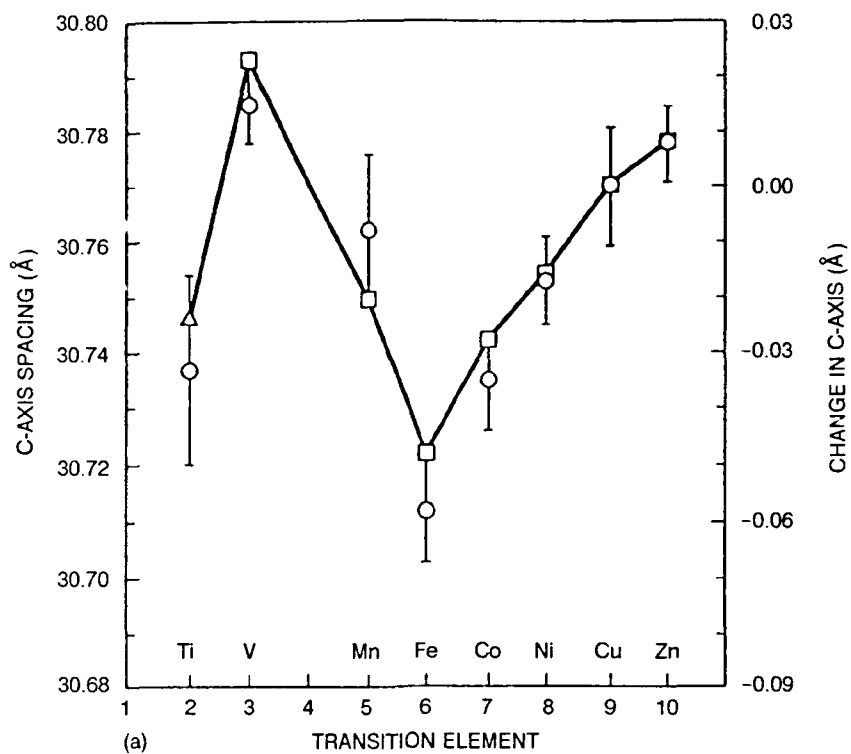
Figure 3. The c-axis lattice parameter for (a)
$Bi_2Sr_2Ca(Cu_{0.95}M_{0.05})_2O_8$ and $Bi_2Sr_2Ca_2(Cu_{0.95}M_{0.05})_3O_{10}$
where M is a transition element.

The effect of these substitutions on the resistive superconducting transition temperature for the $Bi_2Sr_2CaCu_2O_8$ phase is illustrated in figure 4, where the normalized resistance is plotted versus absolute temperature. Note that the control sample has the highest T_c, near 80 K. The small dip in resistance over 100 K is due to a very small amount of the higher T_c phase present in the material. This is most noticeable for the Ti sample. Note also that, with the exception of the Fe sample, the transition widths are as narrow for the modified materials as for the control. Similarly, the resistive superconducting transition for the $Bi_2Sr_2Ca_2Cu_3O_{10}$ phase is illustrated in figure 5, where the normalized resistance is plotted versus absolute temperature. Again, the control sample has the highest T_c, and all the modified materials have transition widths comparable to the control.

One difficulty in substituted materials of this type is that the substituent may not go into the structure uniformly. This usually manifests itself in broadened transitions relative to the control sample. In this case, the sharpness of the transitions implies that the substitutions are very homogeneous.

The superconducting transitions of all these materials were also measured inductively, either with a Faraday balance or with a SQUID magnetometer. The inductively measured T_c for Zn substituted $Bi_2Sr_2CaCu_2O_8$ is illustrated in figure 6, where the volume susceptibility, measured with a Faraday balance in a magnetic field of 200 Gauss, is plotted versus absolute temperature. The onset of a large negative diamagnetic response, characteristic of superconductivity, is seen near 67 K. The warming curve was taken after cooling the sample in zero magnetic field, applying the 200-Gauss field, and warming through the transition. This is the "shielding" curve. The cooling curve was taken in the 200-Gauss field, applied when the sample was above the transition, then cooled through the superconducting transition. This large diamagnetic response at T_c is caused by the flux being expelled from the sample (Meissner effect).

All the data described above are summarized in tables 2 and 3, where the transition temperatures measured resistively (midpoints) and inductively (onsets) are listed, along with the transition width ($\pm T_c$) determined from the resistive measurements. The temperature where the resistance goes to zero (R = 0) is also listed. The transition temperatures determined resistively and inductively are usually somewhat different in this type of sample because they measure different portions of the sample. The resistance measures the lowest resistance percolation path through the sample, whereas the inductance measures more of a volume average susceptibility.
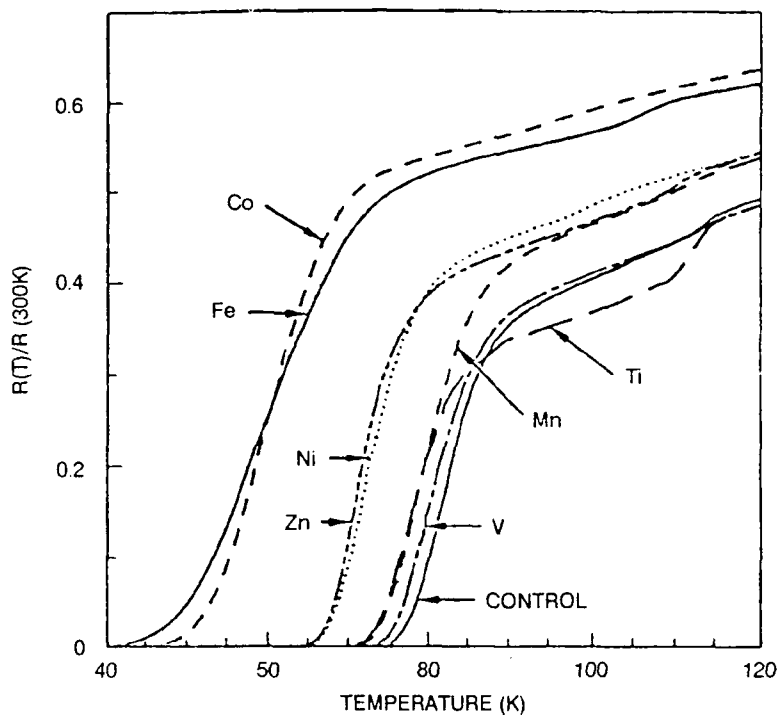
12

Figure 4. Normalized resistance versus absolute
temperature for $Bi_2Sr_2Ca(Cu_{0.95}M_{0.05})_2O_8$.
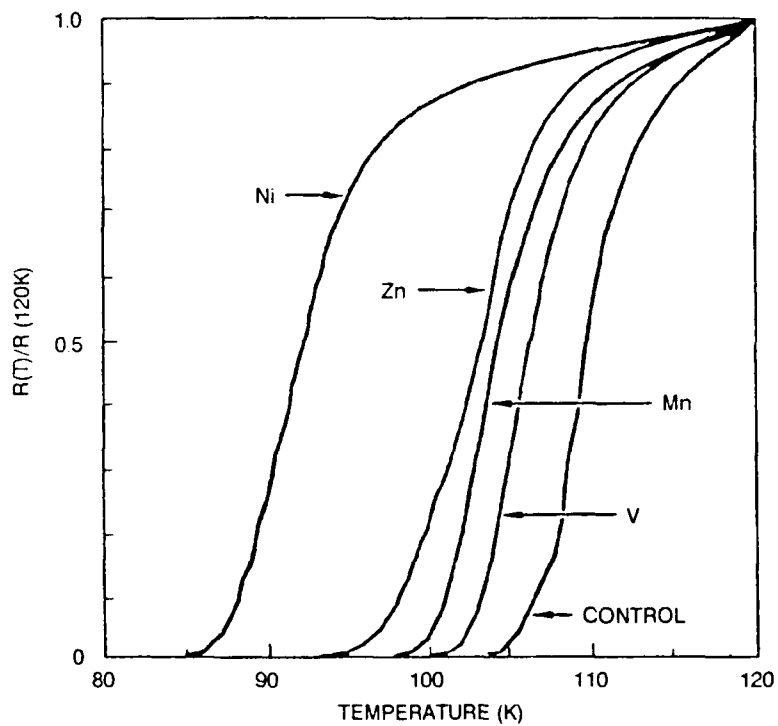
Figure 5. Normalized resistance versus absolute
temperature for $Bi_2Sr_2Ca_2(Cu_{0.95}M_{0.05})_3O_{10}$.

13

Table 2. Superconducting transition temperatures for substituted $Bi_2Sr_2CaCu_2O_8$.

Replacement Element (5 mole-% for Cu)	Resistive Transition (Midpoint (K))	$\pm T_c$ (K)	R = 0 (K)	Inductive Transition (K)
Control	82	5	74	80
V	81	7	73	80
Mn	80	6	71	79
Ti	78	6	71	75
Ni	73	6	65	69
Zn	71	5	64	67
Co	60	7	47	65
Fe	60	11	43	65

Table 3. Superconducting transition temperatures for substituted $Bi_2Sr_2Ca_2Cu_3O_{10}$.

Replacement Element (5 mole-% for Cu)	Resistive Transition (Midpoint (K))	$\pm T_c$ (K)	R = 0 (K)	Inductive Transition (K)
Control	109	4	104	105
V	105	4	101	110
Mn	105	7	95	106
Ti	103	5	98	105
Zn	102	6	95	105
Ni*	91	6	86	93

*The nickel sample is mixed phase (90% $Bi_2Sr_2Ca_2Cu_3O_{10}$/10% of $Bi_2Sr_2CaCu_2O_8$).
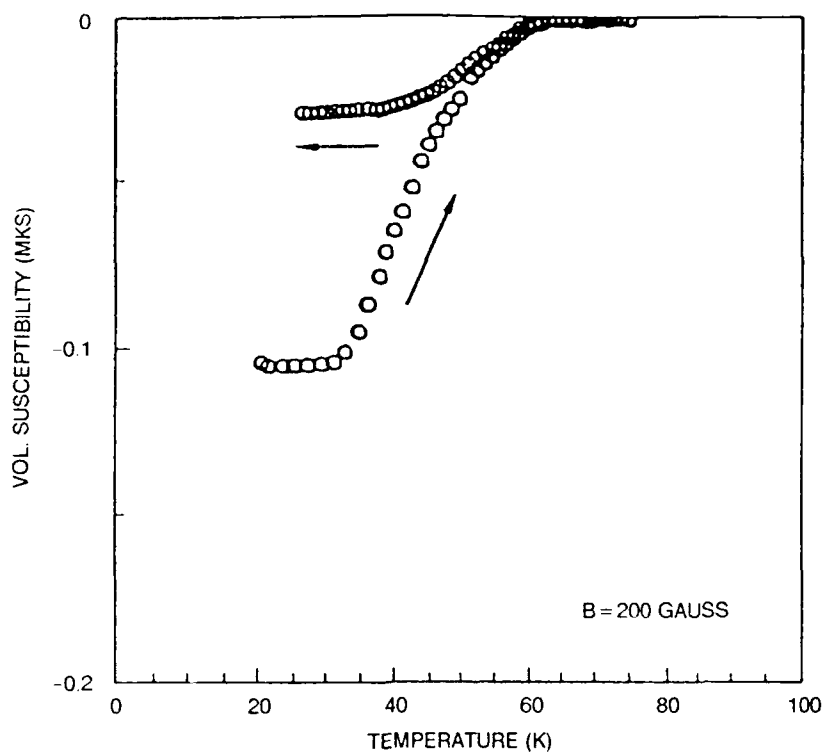
Figure 6. Volume magnetic susceptibility versus absolute temperature for Zn substituted $Bi_2Sr_2CaCu_2O_8$.

One interesting property of the transition row elements is that they have different magnetic moments as electrons fill the '3d' orbitals. For conventional low-temperature superconductors, magnetic moments have been shown to have a severe pair-breaking effect on superconductivity (Jones, 1977). To determine the effective magnetic moments of the substituent spins in this system, the magnetic moments were measured with a Faraday balance. This is illustrated in figure 7 for the Mn substituted $Bi_2Sr_2Ca_2Cu_3O_{10}$, where the inverse susceptibility is plotted versus absolute temperature. For a Curie system (free spins), this should be a straight line whose slope yields the magnetic moment (assuming one knows the concentration). From the slope in figure 7, and the known concentration, one readily calculates that the average total angular momentum, J, of each Mn spin in this system is two ($J = 2$). Similar measurements were made on all the samples.

The accuracy of the magnetic moment determination depends in part on knowing the actual concentration of substituent in the sample. The samples were all made to a nominal 5.0 mol.-% for Cu level. However, long sintering times near the melting temperature could volatize components. In any case, an independent elemental analysis of the sample composition is highly desirable in this type of investigation. These samples

15

were all analyzed by a technique called Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The results of the elemental analysis for both phases are illustrated in table 4. As is evident from the table, the final concentrations of the substituents are very near the nominal concentration, averaging approximately 2.5% high.

Table 4. Results of elemental analysis of the samples via the Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) technique.

| | Mole-% for Cu by ICP Analysis | |
Dopant	$Bi_2Sr_2CaCu_2O_8$	$Bi_2Sr_2Ca_2Cu_3O_{10}$
Ti	5.06	4.96
V	4.84	5.17
Mn	5.38	5.42
Fe	4.92	4.99
Co	5.15	5.13
Ni	5.24	5.60
Zn	4.93	5.09

Mean result for all samples: 5.13 ± 0.22 mole-%.

The corrected concentrations as determined by the above analysis were used to refine the angular momentum (J) data discussed above. Further, knowing the number of '3d' electrons and the total spin, a tentative assignment can be made of the electrons to the five different crystal-field-split energy levels appropriate for the square pyramidal symmetry of the copper sites. This has been done, and the results are illustrated in table 5. The number of '3d' electrons are shown (1st column) for the appropriate cation (2nd column). The value of 'J' experimentally determined (5th column) is shown along with the nearest half-integer momentum value possible (4th column). Electron occupancy for the crystal-field energy levels are shown (3rd column) that are consistent with the above information.
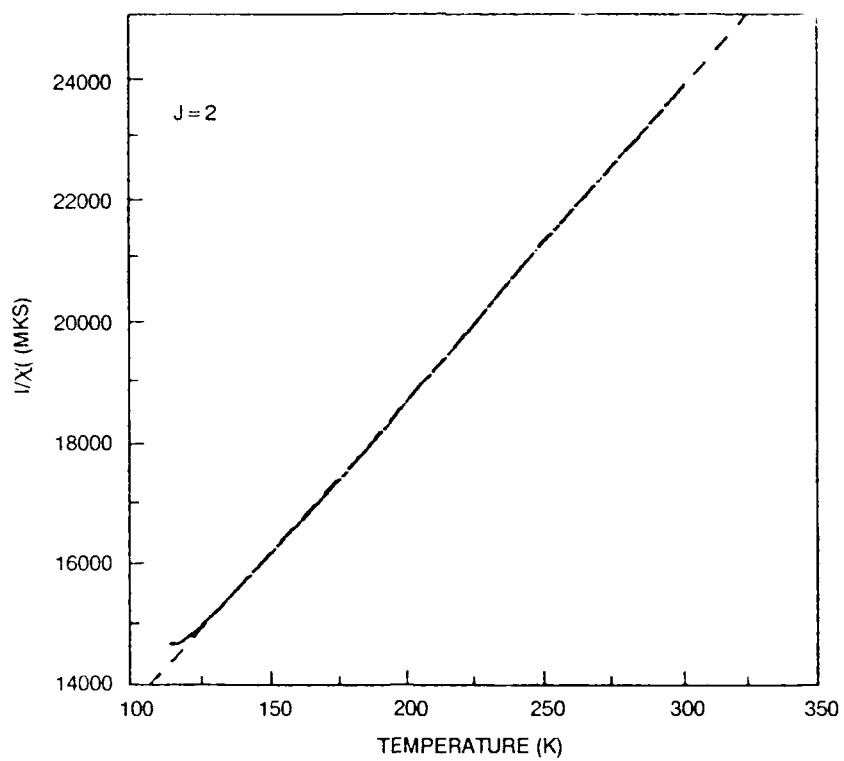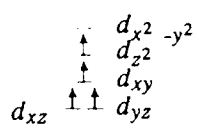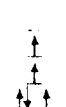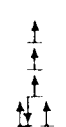
16
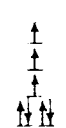
Figure 7. Inverse volume susceptibility versus absolute temperature for Mn substituted $Bi_2Sr_2Ca_2Cu_3O_{10}$.

Table 5. Spin states for those cations having the largest angular momentum as determined by magnetic-susceptibility measurements.

# of '3d' Electrons	Cation	Crystal Field Splitting	'J'	'J' Exp.
4	Mn^{3+}	d_{xz} ↑ ↑ d_{yz} ↑ d_{xy} ↑ d_{z^2} ↑ $d_{x^2-y^2}$	2	1.95
5	Mn^{2+}	↑ ↑ ↑↑ ↑	3/2	1.6
6	Fe^{2+}	↑ ↑ ↑ ↑↓ ↑	2	1.85
7	Co^{2+}, Ni^{3+}	↑ ↑ ↑ ↑↓ ↑↓	3/2	1.6, 1.4
8	Ni^{2+}	↑ ↑ ↑↓ ↑↓ ↑↓	1	0.9

CONCLUSIONS

Several observations can be made when studying the summary tables for the reduction in T_c for substituted $Bi_2Sr_2CaCu_2O_8$ (table 2) and $Bi_2Sr_2Ca_2Cu_3O_{10}$ (table 3). In both cases, the vanadium substitution had the least harmful effect on T_c. For the $Bi_2Sr_2Ca_2Cu_3O_{10}$ phase, the inductively measured transition temperature was even raised slightly. This effect was reproducible but not understood. The effectiveness of the dopants, as far as suppressing T_c for $Bi_2Sr_2CaCu_2O_8$, in order of increasing suppression of T_c, are $V^{2+}, Mn^{2+}, Ti^{3+}, Ni^{2+}, Zn^{2+}, Co^{2+}$, and Fe^{2+}. For $Bi_2Sr_2Ca_2Cu_3O_{10}$, the order is $V^{3+}, Ti^{3+}, Mn^{3+}, Zn^{2+}$, and Ni^{3+}. The valence state is derived from the x-ray diffraction results of figure 3.

So what properties of the transition element correlate with T_C? Before answering that question, it is instructive to discuss three properties that one might expect to correlate with T_C, *but that do not correlate with T_C*.

First, the T_C does not correlate with the position of the transition element in the periodic table; that is, T_C is not correlated with either the number of '3d' electrons or with the ionic radius. This is interesting because some models would predict a correlation based on atomic size. A smaller lattice allows more overlap of the electronic wave functions, and a potentially stronger attractive interaction between electrons.

Second, T_C is not correlated with the observed magnetic moment of the cation. This is also surprising because in the older superconductors the effect of magnetic moments is well studied and understood. A local magnetic moment breaks the superconducting pair because each member of the pair (usually one spin up and one spin down) sees a different scattering potential at the impurity spin site. Generally, this interaction suppresses T_C linearly at low concentrations. A few percent of iron can have catastrophic effects on superconductivity in conventional superconductors.

Third, T_C does not correlate with the ionization potential of the cation. One might expect such a correlation because some theories offer a partial explanation of high T_C superconductivity as being due, in part, to a balance between the ionization potential of copper and the electron affinity of oxygen in this structure. The closer these two energies, as the theory goes, the less energy it takes for the electrons to move and, consequently, the pair mobility in the planes is increased. Disturbing this balance by substitutions described here might gradually reduce the superconducting properties in a systematic way.

Finally, *a strong correlation is found between T_C and the occupancy of the $d_{x^2-y^2}$ orbital.* Referring to tables 2, 3, and 5, the suppression of T_C is greatest for Fe^{2+} (iron in $Bi_2Sr_2CaCu_2O_8$), Co^{2+} (cobalt in $Bi_2Sr_2CaCu_2O_8$), Ni^{3+} (nickel in $Bi_2Sr_2Ca_2Cu_3O_{10}$), and Ni^{2+} (nickel in $Bi_2Sr_2CaCu_2O_8$). These cations all have electrons in the $d_{x^2-y^2}$ orbital.

Why should the occupancy of the $d_{x^2-y^2}$ orbital be a critical factor? The $d_{x^2-y^2}$ orbital is the highest energy '3d' orbital and, consequently, its occupancy is quite variable and important. Furthermore, the copper $d_{x^2-y^2}$ orbital is the only copper orbital that has the proper symmetry to form a molecular bond with the oxygen p_x and p_y orbitals in the copper-oxygen planes. Indeed, band structure calculations have shown that this is the case (Hybertsen & Mattheiss, 1988), resulting in an extended planar molecular orbital. Because the superconductivity of these materials has been shown to be hole-type, these hybridized hole states must contain the carriers responsible for superconductivity in these materials. It should, therefore, be expected that any substitution that affects the occupancy of this orbital will have an extreme effect on the superconducting properties.

PLANS

The research described in this article, and most of the other work performed on this project, was conducted on bulk-sintered materials. The emphasis of future work at NOSC will be on thin superconducting films of these materials for electronic applications. The techniques of ion-assisted ion beam cosputtering and plasma-assisted chemical vapor deposition will be used to grow layered thin-film structures of high T_c superconductors for electronic applications and to study interfaces between the layers.

REFERENCES

Bardeen, J., L.N. Cooper, and J.R. Schrieffer. 1957. *Physical Review B*, vol. 106, p. 162; see also *Physical Review* B, vol. 108, p. 1175.

Bednorz, J.G. and K.A. Muller. 1986. "Possible High T_c Superconductivity in the Ba-La-Cu-O System," *Z. Physica B – Condensed Matter*, vol. 64, p.189.

Chu, C.W., J. Bechtold, L. Gao, P.H. Hor, Z.J. Huang, R.L. Meng, Y.Y. Sun, Y.Q. Wang, and Y.Y. Xue. 1988. "Superconductivity up to 114 K in the Bi-Al-Ca–Sr-Cu-O Compound System with Rare-Earth Elements," *Physical Review Letters*, vol. 60, no. 10, p. 941.

Gorter, C.J., 1964. *Review of Modern Physics*, vol 36, p. 1.

Green, R.L., G.B. Street, and L.J. Suter. 1975. *Physical Review Letters*, vol. 34, p. 577.

Hybertsen, S. and L.F. Mattheiss. 1988. "Electronic Band Structure of $CaBi_2Sr_2Cu_2O_8$, " *Physical Review Letters*, vol. 60, no. 16, p. 1661.

Jones, T.E., *The Compensation Effect and Re-Entrant Superconductivity in a Magnetically Ordered Superconductor*. 1977. Thesis, University of California, Los Angeles, CA.

Jones, T.E., P.M. Thibado, R.D. Boss, W.C. McGinnis, and S. Oseroff. 1990. "Partial Substitution of Transition Row Elements for Copper in $Bi_2Sr_2CaCu_2O_8$ and $(Bi, Pb)_2Sr_2Ca_2Cu_3O,_{10}$ – Superconducting Properties," *Bulletin of the American Physical Society*, vol. 35, no. 3, p. 788.

Jones, T.E., P.M. Thibado, W.C. McGinnis, R.D. Boss, J.W. Schindler, and S. Oseroff. 1989. "Substitutions of 3–D Transition Metal Ions for Copper in $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, " Physica C, vol. 25, pp. 162–164.

Kittel, C. 1971. *Introduction to Solid State Physics*, ch. 12, 4th edition, John Wiley & Sons, New York, NY.

Onnes, H.K. 1911. *Akad. van Wetenschappen* (Amsterdam), vol. 14, 113, 818.

Ribault, M., P.M. Chaikin, G. Montambaux, and M. Herritier. 1987. *Low-Dimensional Conductors and Superconductors*, D. Jerome and L.G. Caron, Eds, NATO Advanced Study Institute, ser. B. vol. 55, Plenum, New York, NY.

Sheng, Z.Z., A.M. Hermann, A. El Ali, C. Almasan, J. Estrada, T. Datta, and R.J. Matson. 1988. "Superconductivity at 90 K in the Tl-Ba-Cu-O System," *Physical Review Letters*, vol. 60, no. 10, p. 937.

Thibado, P.M., T.E. Jones, R.D. Boss, W.C. McGinnis, and S. Oseroff. 1990. "Partial Substitution of Transition Row Elements for Copper in $Bi_2Sr_2CaCu_2O_8$ and $(Bi, Pb)_2Sr_2Ca_2Cu_3O_{10}$ – Sample Preparation and X-ray Structure," *Bulletin of the American Physical Society*, Vol. 35, no. 3, p. 788.

Wu, M.K., J.R. Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Y.Q. Wang, and C.W. Chu. 1987. "Superconductivity at 92 K in a New Mixed-Phase Y-Ba-Cu-O Compound System at Ambient Pressure," *Physical Review Letters*, vol. 58, no. 9, p. 908.

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1 AGENCY USE ONLY *(Leave blank)*	2 REPORT DATE August 1991	3 REPORT TYPE AND DATES COVERED Final

4 TITLE AND SUBTITLE
A REVIEW OF HIGH-TEMPERATURE SUPERCONDUCTIVITY AND THE EFFECT OF CHEMICAL MODIFICATIONS ON $Bi_2Sr_2CaCu_2O_8$ and $Bi_2Sr_2Ca_2Cu_3O_{10}$

5 FUNDING NUMBERS

PE: 0601152N
WU: DN 308045

6 AUTHOR(S)
T. E. Jones, W. C. McGinnis, R. D. Boss, Naval Ocean Systems Center and
P. M. Thibado, University of Pennsylvania

7 PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Naval Ocean Systems Center
San Diego, CA 92152–5000

8 PERFORMING ORGANIZATION REPORT NUMBER

TR 1441

9 SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Chief of Naval Research
Arlington, VA 22217–5000

10 SPONSORING/MONITORING AGENCY REPORT NUMBER

11 SUPPLEMENTARY NOTES

12a DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b DISTRIBUTION CODE

13 ABSTRACT *(Maximum 200 words)*

This report documents the chemical modifications made to existing materials that may enhance their superconducting properties and provides insight into the mechanisms responsible for high-temperature superconductivity.

14 SUBJECT TERMS		15 NUMBER OF PAGES 29
copper oxide T_c vanadium ceramic oxide		16 PRICE CODE

17 SECURITY CLASSIFICATION OF REPORT	18 SECURITY CLASSIFICATION OF THIS PAGE	19 SECURITY CLASSIFICATION OF ABSTRACT	20 LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAME AS REPORT

NSN 7540-01-280-5500

Standard form 298

21a. NAME OF RESPONSIBLE INDIVIDUAL	21b. TELEPHONE *(include Area Code)*	21c. OFFICE SYMBOL
T. E. Jones	(6 9)553-1594	Code 633

INITIAL DISTRIBUTION

Code 0012	Patent Counsel	(1)
Code 014	W. Rasmussen	(1)
Code 0141	A. Gordon	(1)
Code 0142	K. Campbell	(1)
Code 0143	B. Kolesar	(1)
Code 0144	R. November	(1)
Code 50	H. Porter	(1)
Code 501	P. Fletcher	(1)
Code 57	R. Moore	(1)
Code 573	C. Hicks	(1)
Code 573	T. Jones	(60)
Code 60	F. Gordon	(1)
Code 952B	J. Puleo	(1)
Code 961	Archive/Stock	(6)
Code 964B	Library	(3)

Defense Technical Information Center
Alexandria, VA   22304-6145   (4)

NOSC Liaison Office
Washington, DC   20363-5100

Center for Naval Analyses
Alexandria, VA   22302-0268

Navy Acquisition, Research & Development
     Information Center (NARDIC)
Alexandria, VA   22333